Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO$_2$ process

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Abstract

The use of hydrogen peroxide (H$_2$O$_2$) for improved photocatalytic degradation of phenol in aqueous suspension of commercial TiO$_2$ powders (Degussa P-25) was investigated. Photodegradation was compared using direct photolysis (UV alone), H$_2$O$_2$/UV, TiO$_2$/UV, and H$_2$O$_2$/TiO$_2$/UV processes in a batch reactor with high-pressure mercury lamp irradiation. The effects of operating parameters such as catalyst dosage, light intensity, pH of the solution, the initial phenol, and H$_2$O$_2$ concentrations on photodegradation process were examined. It was shown that photodegradation using H$_2$O$_2$/TiO$_2$/UV process was much more effective than using either H$_2$O$_2$/UV or TiO$_2$/UV process. The effect of the initial phenol concentration on TOC removal was also studied, demonstrating that more than 8 h was required to completely mineralize phenol into water and carbon dioxide. For all the four oxidation processes studied, photodegradation followed the first-order kinetics. The apparent rate constants with 400-W UV ranged from 5.0×10^{-4} min^{-1} by direct photolysis to 1.4×10^{-2} min^{-1} using H$_2$O$_2$/TiO$_2$/UV process. The role of H$_2$O$_2$ on such enhanced photodegradation of phenol in aqueous solution was finally discussed.
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Keywords: Photocatalytic degradation; Phenol; Titanium dioxide; Hydrogen peroxide; UV irradiation

1. Introduction

Heterogeneous photocatalysis is a promising technique to deal with environment pollution. It has been extensively studied during the last 20 years because it is able to totally oxide organic molecules at a low energy cost. The UV irradiation of titanium dioxide (TiO$_2$) upon incidence of photon with an energy higher than its band gap energy (that is, the so-called photoexcitation) results in the formation of electrons (e$^-$) in the conduction band and positive holes (h$^+$) in the valence band, as well as the formation of OH radicals [1]. Photodegradation process is considered to be the reduction of oxygen by the trapped electrons on the surface of semiconductors to produce reduced oxygen species such as superoxide radical ions O$_2{}^-$; these superoxide species have strong oxidization capability. The photogenerated electron–hole pairs can also recombine; thus inhibiting recombination of the electron–hole pairs and prolonging lifetime of the carriers are essential for improving the efficiency of net charge transfer at the semiconductor/electrolyte interface. Hydroxyl ions (OH$^-$) are

the likely traps for holes, leading to the formation of hydroxyl radicals that are strong oxidizing agents, while the adsorbed oxygen species are the traps for electrons, leading to the formation of unstable superoxide species (O$_2{}^-$) [2]. These highly reactive free radicals oxidize organic pollutants present in the system, and eventually mineralize them to carbon dioxide and water [1–3].

Phenolic compounds in aqueous solutions cause severe environmental problems. A representative of this class of compounds is phenol. Sources of phenol include the process or waste solutions in chemical process industries and agriculture production [4]. Hence, extensive studies on photocatalytic degradation of phenols and chlorinated phenols in aerated aqueous suspensions of TiO$_2$ upon illumination with near-UV light have been reported [2,3,5,6]. The commercial Degussa TiO$_2$ P-25 powder, which has a relatively large surface area (55 m^2/g), has been used as standard TiO$_2$ material in the studies of photocatalytic reactions. Bickley et al. [7] have first examined the photocatalytic activity of P-25 and the structural relationship based on TEM pictures. Subsequently, Ohno et al. [8] provided the evidence of synergistic effect between contacting anatase and rutile particles. They indicated that naphthalene is efficiently oxidized in a mixed suspension of both types of TiO$_2$ powders on UV irradiation, and

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found that TiO_2 powders with both anatase and rutile structures have higher activity in photocatalytic reactions. Recently, photocatalytic degradation of organic pollutants using TiO_2 particles has received considerable attention.

Although the effects of various operating parameters such as catalyst dosage, the initial concentrations of organic pollutants, pH, and UV light intensity have been widely investigated [9,10], the improvement of oxidative degradation of organic compounds is still worthy of particular attention for practical applications [11,12]. In fact, the combination of advanced oxidation processes and photochemical reactions including the methods of H_2O_2/UV, TiO_2/UV, H_2O_2/TiO_2/UV, and photo-Fenton or Fenton-like reactions has recently been the subject of numerous studies [2,12–21]. The primary mechanism is the generation of hydroxyl radicals, the species with very high oxidizing capacity (redox potential 2.8 V), and the addition of H_2O_2 preventing the recombination of electrons and holes, thereby the hydroxyl radicals are able to react very rapidly with most of the organic pollutants [13–21].

In this work, the effect of added H_2O_2 on the increased efficiency of photocatalytic oxidation of phenol in aqueous solutions using TiO_2 was examined. To achieve this goal, the photodegradation of phenol should be compared using different irradiation processes such as direct photolysis (UV alone), H_2O_2/UV, TiO_2/UV, and H_2O_2/TiO_2/UV. The optimal degradation conditions under different oxidation conditions were obtained and the apparent first-order rate constants were evaluated and compared.

2. Materials and methods

2.1. Materials and reagents

Phenol (99.5% purity) was purchased from Merck Co. (Germany). All other chemicals used in this work (NaOH, HCl, H_2O_2, etc.) were of reagent-grade quality. Titanium dioxide (P-25, ca. 70% anatase and 30% rutile), offered from Degussa, Germany, has a BET surface area of 55 m^2/g and an average particle size of 30 nm measured by SEM (Hitachi, S-4800, Japan) as shown in Fig. 1. The light source used was a water-cooled 20–400-W high-pressure mercury lamp (HL400EH-5, SEN Japan). The spectral irradiance of the UV lamp ranges from 253.7 to 577 nm, and the illumination distance is 80 mm. The light intensity of UV lamp used for degradation experiments was recorded with an UV/visible spectrophotometer (Shimadzu, UV-2501PC).

2.2. Photodegradation experiments

Photodegradation experiments were conducted in a batch photoreactor (Fig. 2). This small-scale system contained a cylindrical Pyrex-glass cell with 1.0 L capacity (100 mm i.d., 200 mm height). Otherwise stated elsewhere, a 400-W high-pressure mercury lamp was placed in a 50-mm diameter quartz tube. The lamp and tube were then immersed in the photoreactor cell with a light path of 80 mm. The reactor was filled with 0.8 L of phenol solution (0.13–1.01 mM), to which Degussa TiO_2 P-25 powders
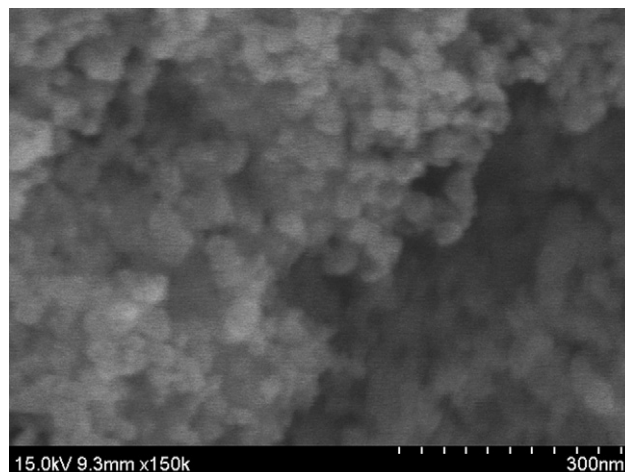

Fig. 1. SEM picture of TiO_2 P-25 particles.

(0–4.0 g/L), H_2O_2 (1.77–88.2 mM), or both were added. The pH value of aqueous solution was adjusted by adding small amount of 0.1 M NaOH or HCl, and was monitored by a digital pH meter (Horiba F-23, Japan). The temperature of the whole photoreactor was kept constant at $25 \pm 0.2\,^\circ$C with a water-cooling jacket around its outside. The suspended solution was kept uniform by agitation with a magnetic stirrer. To maintain an aerobic environment, the compressed air was purged into the solution by bubbling it from the bottom. All the experiments, with or without H_2O_2, were performed under similar conditions at a phenol concentration of 0.51 mM, except that three different UV light intensities were used (20-W low-pressure, 100-W, and 400-W high-pressure mercury lamps).

Solutions were irradiated by UV–vis light. Experiments were conducted for 180 min and the liquid samples (5 mL) were withdrawn at preset time intervals (every 30 min). If TiO_2 powders were present in the system, the samples were subjected to filtration through a 0.2 μm syringe filter (Millipore, cellulose acetate membrane) to remove fine particles before HPLC analysis of phenol concentration. The column employed was
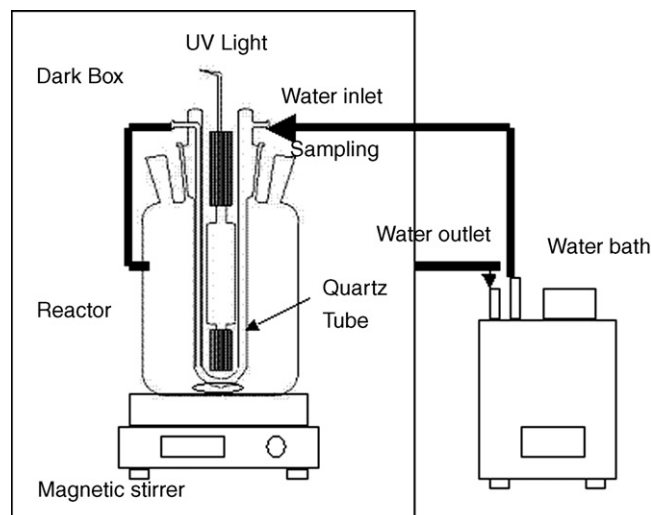

Fig. 2. Schematic representation of the photoreactor.

the Merck LichroCART 250-4 (250 mm length, 4 mm diameter), packed with LiChrospher 100 RP-18e. A mixture of acetonitrile (70%, v/v) and deionized water, flowing at a rate of 1.0 mL/min, was used as the mobile phase. An aliquot of the sample (50 μL) was injected using a Rheodyne valve and analyzed at a wavelength of 270 nm with an UV detector (Perkin Elmer 200). Each experiment was duplicated at least under identical conditions. The reproducibility of concentration measurements was mostly within 4%. The total organic carbon (TOC) of the sample was also analyzed with an OI-Analytical 1010 analyzer.

3. Results and discussion

3.1. Effect of operating parameters on phenol photodegradation

Preliminary experiments had shown that, after 24-h contact, no detectable amount of phenol (initially 0.51 mM) was adsorbed on the surface of P-25 TiO_2 particles (1 g/L) at pH 6.8 [22], likely due to the effect of electrostatic repulsion. However, two possible intermediates during phenol photodegradation, catechol and pyrogallol, could be quickly adsorbed (within 1 min) on the surface of P-25 TiO_2 [21]. It was actually found that white P-25 TiO_2 powders become light yellow upon the contact of TiO_2 with colorless aqueous catechol or pyrogallol solution [22].

Fig. 3 compares the photodegradation of 0.51 mM phenol in aqueous solutions under various reaction conditions. Direct photolysis of phenol with 400-W UV alone leads to an extremely low phenol removal. Also, about 60% of phenol is degraded within 180 min when 1.77 mM H_2O_2 is added. The same efficiency (56%) is obtained when the solution is treated with 1 g/L TiO_2 catalyst under UV irradiation. On the other hand, the combination of such two processes (that is, the $H_2O_2/TiO_2/UV$ system) further improves phenol removal up to 94%. These results are consistent with those reported by other researchers [17–19,21,23]. The possible reactions involving H_2O_2 occur in
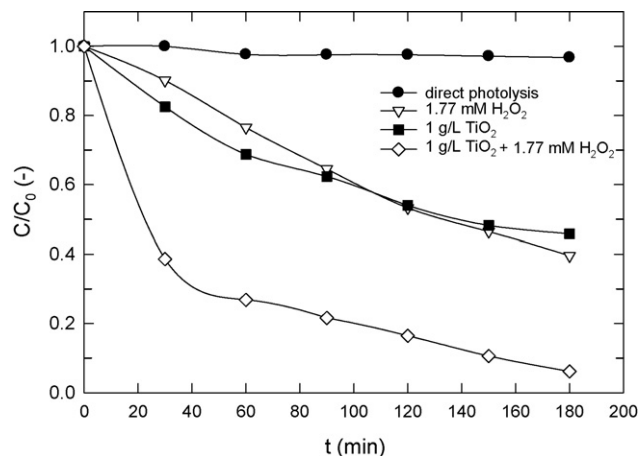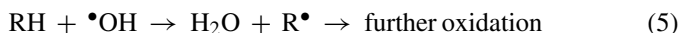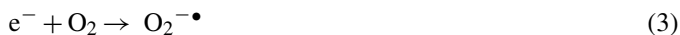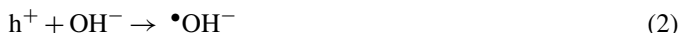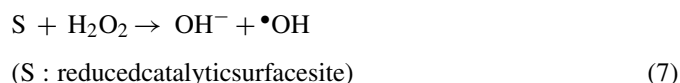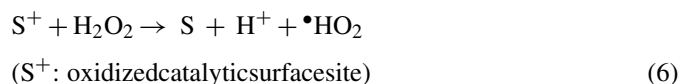

Fig. 3. Effect of various oxidation conditions on phenol removal at 25 °C ($C_0 = 0.51$ mM, initial pH 6.8).

the H_2O_2/UV system can be summarized as follows [20]:

$$H_2O_2 + hv \rightarrow 2^\bullet OH \tag{1}$$

$$h^+ + OH^- \rightarrow {}^\bullet OH^- \tag{2}$$

$$e^- + O_2 \rightarrow O_2^{-\bullet} \tag{3}$$

$$e^- + H_2O_2 \rightarrow HO^\bullet + OH^- \tag{4}$$

$$RH + {}^\bullet OH \rightarrow H_2O + R^\bullet \rightarrow \text{further oxidation} \tag{5}$$

where RH refers to phenolic compound.

The direct photolysis of H_2O_2 by UV light can generate $^\bullet OH$ radical (Eq. (1)), which is a crucial step in improving the rate of photocatalytic reaction. Other mechanisms proposed by Chen et al. [17] and Barakat et al. [20] suggest that H_2O_2 is a better electron acceptor than oxygen. This hence would decrease the chances of an electron/holes recombination. In other words, the hydroxyl radicals formed by the photolysis of H_2O_2 may likely to react with the holes generated during excitation, which in turn will reduce the probability to undergo electron–hole recombination as shown in Eq. (4). The superoxide radical ($^\bullet O_2^-$), as indicated in Eq. (3), as the result, is less dominant in affecting the rate of photocatalytic reaction as compared with hydroxyl radicals according to the mechanism proposed by Chen et al. [17] and Barakat et al. [20]. Furthermore, the reaction mechanism of H_2O_2 at the surface has been proposed by Miller and Valentine [24]. In their model, a single rate-limiting step controlling H_2O_2 loss and ultimately contaminant degradation was incorporated. The surface reaction mechanisms are as follows:

$$S^+ + H_2O_2 \rightarrow S + H^+ + {}^\bullet HO_2$$
$$(S^+: \text{oxidized catalytic surface site}) \tag{6}$$

$$S + H_2O_2 \rightarrow OH^- + {}^\bullet OH$$
$$(S: \text{reduced catalytic surface site}) \tag{7}$$

$$S^+ + O_2^- \rightarrow S + O_2 \tag{8}$$

$$S + {}^\bullet OH_2 \rightarrow S^+ + HO_2^- \tag{9}$$

$$S + {}^\bullet OH \rightarrow S^+ + OH^- \tag{10}$$

In this model, the generation of superoxide and hydroxyl radicals, scavenging reactions of oxygen radicals with the catalytic surface, and contaminant degradation by reaction with hydroxyl radicals which are formed from both surface and solution reactions is proposed. Hydrogen peroxide reacting with both oxidized and reduced surface sites is shown in Eqs. (6) and (7). The reactions of superoxide and perhydroxyl with the catalytic surface are shown in Eqs. (8) and (9), but some escape from scavenging is possible. Hydroxyl radical scavenged by the catalytic surface is also possible as shown in Eq. (10).

Fig. 4 illustrates that the mineralization of phenol by TiO_2/UV and H_2O_2/UV are nearly identical at a reaction time of 180 min (34%), regardless of the pathways. Based on these TOC data, phenol removal by TiO_2/UV and H_2O_2/UV can be divided into two stages. The first stage is a lag state in the
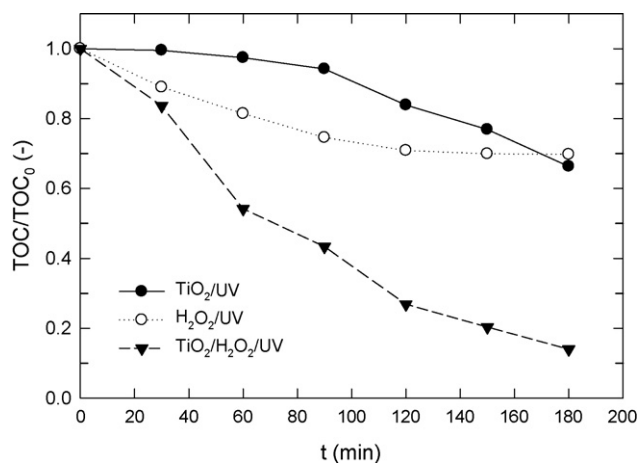
Fig. 4. Effect of various oxidation conditions on TOC removal during phenol removal at 25 °C ($C_0 = 0.51$ mM, initial pH 6.8).

Table 1
Kinetic parameters for phenol degradation at 25 °C using various oxidation methods under the irradiation of 400-W UV ($C_0 = 0.51$ mM)

System	k_{app} (min^{-1})	Initial rate (μM/min)	Half life (min)
Direct photolysis	5.0×10^{-4}	0.225	1380
H$_2$O$_2$/UV (1.77 mM H$_2$O$_2$)	4.9×10^{-3}	0.235	140.8
TiO$_2$/UV (1 g/L TiO$_2$)	4.3×10^{-3}	0.219	160.5
H$_2$O$_2$/TiO$_2$/UV (1 g/L TiO$_2$, 1.77 mM H$_2$O$_2$)	1.4×10^{-2}	0.714	49.3

system reveals a nearly three-fold increase of the reaction rate compared to the TiO$_2$/UV system. That is, the decomposition is mainly contributed by the hydroxyl radicals produced in the presence of H$_2$O$_2$ in the TiO$_2$/H$_2$O$_2$/UV system. On the other hand, 56% of phenol is removed under UV irradiation in the heterocatalytic system (Fig. 3), indicating that the photodegradation is primarily due to the direct action of irradiating TiO$_2$.

3.2. Effect of TiO$_2$ dosage on phenol photodegradation

The dosage of catalyst is an important parameter in suspended photocatalytic degradation processes [5,11]. To determine the optimal dosage of photocatalyst, various amounts of P-25 TiO$_2$ (0–4.0 g/L) were used to mix with 0.51 mM phenol solution. Fig. 5 shows the results at pH 6.8 within 60 min. It is found that UV irradiation in the absence of TiO$_2$ catalyst (i.e., direct photolysis) shows extremely low phenol removal (about 4%). When TiO$_2$ dosage increases from 0.25 to 2 g/L, phenol photodegradation increases from 28 to 43%; however, further increase in TiO$_2$ dosage results in a slight decrease in phenol removal to 36%. This indicates that phenol photodegradation by direct photolysis (using UV alone) is much lower than that of photocatalytic degradation by TiO$_2$. In other words, TiO$_2$ is capable of promoting the interaction between hydroxyl radicals and phenol.

Many studies have demonstrated that the rates of photodegradation for organic pollutants are strongly affected by the number of active sites and the photo-absorption ability of

TiO$_2$/UV system, where TOC reduction is slow. Because phenol photodegradation is likely initiated by branch dissociations, benzene rings remain intact and the hydroxyl radicals produced by the system tend to react with organic molecules over the catalyst surface or in the solution released from the catalyst surface; thereby resulting in an initially slow photodegradation. After the end of the lag state (60 min), a fast-degradation second stage follows. On the contrary, the H$_2$O$_2$/UV system begins with a fast-degradation first stage (90 min) followed by a rather slow second stage. It is believed that the slow second stage is due to the loss in the effectiveness of hydroxyl radicals due to saturation. However, the fact that TOC remains nearly constant does not mean absence or low photodegradation since other intermediates may also exist as the result of photodegradation (i.e., hydroquinone, catechol, formate, acetate, etc.). For the H$_2$O$_2$/TiO$_2$/UV system, TOC removal is greatly accelerated; with 87% of the TOC being mineralized after 180 min of reaction. Thus, combining H$_2$O$_2$/UV with TiO$_2$/UV further enhances photodegradation for organic pollutants than H$_2$O$_2$/UV or TiO$_2$/UV alone.

The Langmuir–Hinshelwood model is usually used to describe the kinetics of photocatalytic reactions of aquatic organics [3,12,15,25]. It basically relates the degradation rate (r) and the concentration of organic compound (C), which is expressed as follows:

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C}$$

(11)

where k_r is the intrinsic rate constant and K_{ad} is the adsorption equilibrium constant. When the adsorption is relatively weak and/or the concentration of organic compound is low, Eq. (11) can be simplified to the first-order kinetics with an apparent rate constant k_{app}:

$$\ln\left(\frac{C}{C_0}\right) = -k_r K_{ad} t = -k_{app} t$$

(12)

A plot of $-\ln(C/C_0)$ versus reaction time t yields a straight line, and the slope is the apparent rate constant.

Table 1 lists the kinetic parameters for phenol photodegradation under various oxidation conditions. The H$_2$O$_2$/TiO$_2$/UV
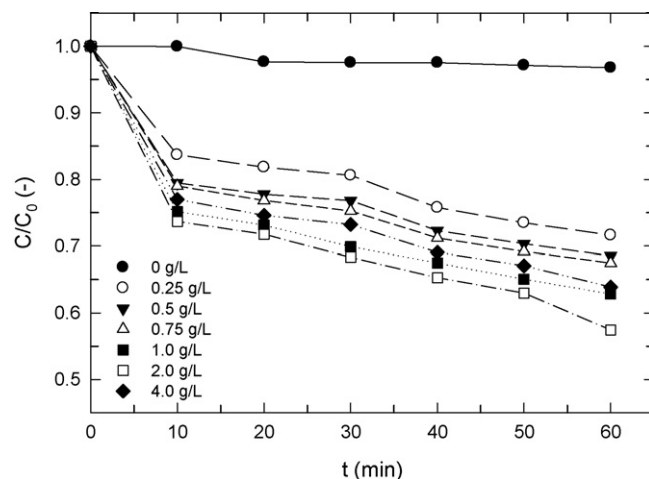

Fig. 5. Effect of the dosage of TiO$_2$ catalyst on phenol removal at 25 °C using TiO$_2$/UV process ($C_0 = 0.51$ mM, initial pH 6.8).
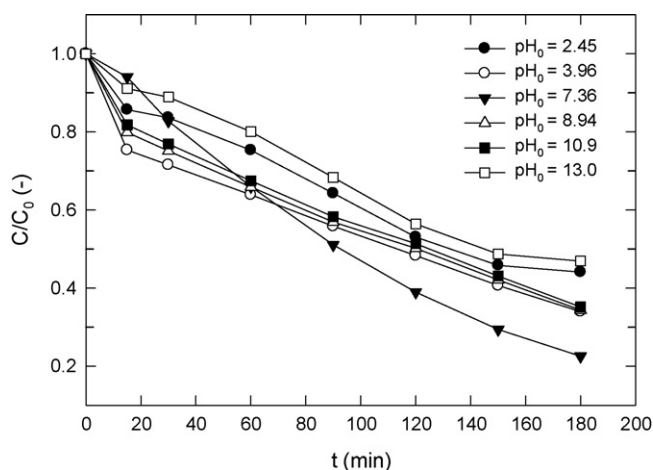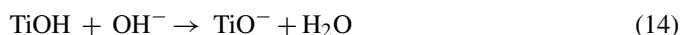
Fig. 6. Effect of the initial phenol concentration on phenol removal at 25 °C using TiO$_2$/UV process (initial pH 6.8, 1 g/L TiO$_2$).

Fig. 7. Effect of the initial phenol concentration on TOC removal during phenol removal at 25 °C using TiO$_2$/UV process (initial pH 6.8, 1 g/L TiO$_2$).

the catalyst used [3]. Adequate dosage of the catalyst increases the generation rate of electron/hole pairs; thus, the formation of OH radicals for enhancing photodegradation. However, an excess dosage of the catalyst decreases the light penetration *via* shielding effect of the suspended particles [23,26] and hence reduces photodegradation rate. According to the results of phenol removal (Fig. 5), the TiO$_2$ dosage of 1–2 g/L reveals comparable performance at 60 min. Hence, a dosage of 1.0 g/L is selected for further studies.

3.3. Effect of the initial phenol concentration on photodegradation

The photodegradation of phenol at different initial concentrations ($C_0 = 0.13$–1.01 mM) in the TiO$_2$/UV system are compared in Fig. 6. The fraction of unreacted phenol (C/C_0) increases with increasing C_0 under the conditions studied; however, the total amount of phenol degraded actually increases. The limited number of surface sites of the TiO$_2$ catalyst may control phenol photodegradation. At a phenol concentration below 0.13 mM, more than 90% of phenol is removed within 1 h. The present results indicate that photocatalytic oxidation is rather promising at low organic pollutant concentrations. This is also the case for heterogeneous catalytic processes where the reaction occurs at the interface between the two phases. Fig. 7 shows the effect of the initial phenol concentration on TOC removal. Evidently, the removal rate decreases with increasing C_0. Unlike the fact that phenol removal is nearly completed within 1 h at $C_0 = 0.13$ mM (Fig. 6), the TOC results show a fast reaction rate at the first 2 h in reaching 30% degradation and a slow reaction rate after 6 h. The removal of TOC reaches 92% within 8 h, and more time is required to completely mineralize phenol into water and carbon dioxide. This behavior could be reflected by its complicated reaction mechanism of phenol oxidation in the presence of illuminated TiO$_2$ and H$_2$O$_2$ [26], as shown in Fig. 8.

A Langmuir–Hinshelwood type of kinetic expression is still adopted here to describe the concentration effect on its photodegradation rate [26,27]. Table 2 lists the apparent rate

Fig. 8. The possible reaction mechanism of phenol oxidation in the presence of illuminated TiO$_2$ [26].

constant k_{app} and the correlation coefficient for phenol photodegradation at different concentrations. It is found that the linear relationship is good.

3.4. Effect of pH on phenol photodegradation

Fig. 9 shows the influence of solution pH on phenol photodegradation ($C_0 = 0.51$ mM) in the TiO$_2$/UV system. The pH of the solution dominates photodegradation process due to the strongly pH dependent of the properties such as semiconductor's surface charge state, flat band potential, and dissociation of the solution. For Degussa P-25 TiO$_2$ used here, the point of zero charge (pH$_{pzc}$) is between 6.25 and 6.60 [28,29]. Thus, the

Table 2
Apparent first-order rate constant k_{app} and correlation coefficient R^2 for phenol degradation at 25 °C and different initial concentrations C_0 (TiO$_2$/UV system, 1 g/L TiO$_2$)

C_0 (mM)	k_{app} (min^{-1})	R^2
0.13	3.5×10^{-2}	0.9957
0.26	2.9×10^{-2}	0.9875
0.51	1.4×10^{-2}	0.9890
0.79	8.9×10^{-3}	0.9784
1.01	3.1×10^{-3}	0.9725

Fig. 9. Effect of the initial solution pH on phenol removal at 25 °C using TiO₂/UV process ($C_0 = 0.51$ mM, 1 g/L TiO₂).

Fig. 10. Effect of the initial H_2O_2 concentration on phenol removal at 25 °C using H_2O_2/UV process ($C_0 = 0.51$ mM, initial pH 6.8).

surface of the catalyst will be positively charged for pH < pH$_{pzc}$, negatively charged for pH > pH$_{pzc}$, and neutral for pH = pH$_{pzc}$:

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad (13)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad (14)$$

where $TiOH_2^+$, TiOH, and TiO^- are the positive, neutral, and negative surface hydroxyl groups, respectively. These characteristics affect significantly not only the adsorption–desorption properties of TiO₂ surface, but also the changes of pollutant structure at various pH values [30]. For example, phenol has a pK_a of 9.95 and can be charged positively or negatively under the pH range studied; i.e., the interaction and affinity between both TiO₂ and phenol will be varied with the solution pH.

The results of Fig. 9 indicate that photodegradation of phenol is not favored in an acidic solution (pH < 3). An increase in solution pH enhances the photodegradation, and reaches a maximum at pH 7.4. However, photodegradation decreases when the pH further increases. The photodegradation efficiency is bound to the distribution of the species of phenol and the state of TiO₂ surface according to pH value and the presence of cations or anions in the solution. At acidic to neutral media, phenol is primarily in its nonionic form; water solubility is minimized and the adsorption onto the catalyst is maximized. The charge attraction between negatively charged phenol molecules and positively charged TiO₂ particles enhances the coupling of phenol molecules with TiO₂ particles. The density of hydroxyl radicals is presumably the highest near the surface of TiO₂ particles and decreases rapidly with distance from the surface. On the other hand, phenol tends to exist as phenolate anions at higher pH values. Such anions have extremely high solubility in solution and will not be adsorbed significantly. Coulombic repulsion between the negatively charged surface of TiO₂ particles and the hydroxide anions could avoid the formation of hydroxyl radicals, hence reducing the photodegradation. At a pH above 11, phenol is completely in the form of phenolate anion and the surface of TiO₂ is at the state of TiOH that should hamper the
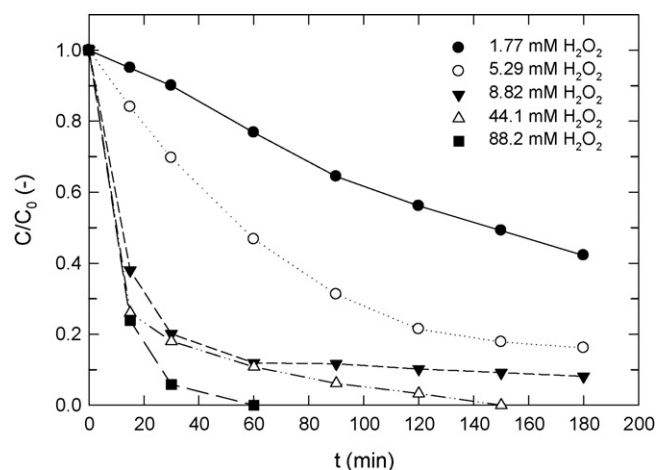
adsorption of negative charges [9,31]. Similar results were also reported by Wei et al. [32] in the photodegradation of phenol using TiO₂ under UV irradiation.

3.5. Effect of added H_2O_2 concentration on phenol photodegradation

The combination of H_2O_2 with UV irradiation has been most exhaustively investigated and the applied technology has been concerns as an advanced oxidation process [12–16]. Through the addition of H_2O_2, a higher OH^- concentration and a more effective mineralization can be attained. The experiments were carried out in the same batch photoreactor as that used in photodegradation experiments. Fig. 10 shows the effect of added H_2O_2 concentrations (1.77–88.2 mM) on phenol photodegradation at pH 6.8 using H_2O_2/UV process. It is evident that the degradation increases with increasing H_2O_2 concentration. The addition of H_2O_2 from 1.77 to 8.82 mM leads to an increase in removal efficiency from 58 to 84% within 3 h. On the other hand, phenol is completely degraded within 2.5 and 1 h when H_2O_2 concentration increases up to 44.1 and 88.2 mM, respectively. In practice, the apparent rate constants (k_{app}), calculated under the H_2O_2 concentration range studied, reveal about 20-fold difference. It is noticed here that no significant drop in photocatalytic degradation (dual effect) is observed with increasing H_2O_2 concentration from 0.2 to 1 M.

The effect of initial phenol concentration C_0 on phenol photodegradation at a fixed H_2O_2 concentration (5.88 mM) is shown in Fig. 11. As also the use of TiO₂/UV system (Fig. 6), photodegradation efficiency decreases with increasing C_0. It is also confirmed in this work that phenol photodegradation using H_2O_2/UV process follows the first-order kinetics [16]. The apparent rate constants are 2.3×10^{-4}, 1.4×10^{-4}, 8.8×10^{-5}, and 3.0×10^{-5} min^{-1} at $C_0 = 0.26$, 0.51, 0.79, and 1.01 mM, respectively. Obviously, the concentration of H_2O_2 plays a crucial role in determining the overall performance of such photodegradation process.
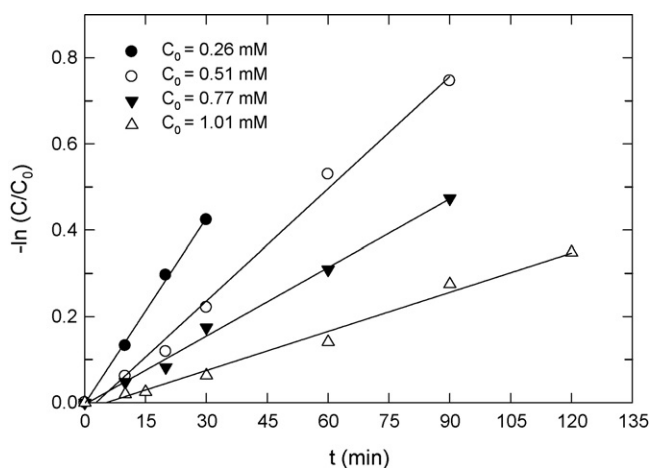
Fig. 11. Rate of phenol degradation at 25 °C and different initial phenol concentrations using H_2O_2/UV process (initial pH 6.8, 5.88 mM H_2O_2).

3.6. Effect of UV light intensity on phenol photodegradation

The effect of UV light intensity (20–400 W) on phenol photodegradation, with or without H_2O_2, was studied in the presence of TiO_2. It is found that all the reactions still follow the first-order kinetics (Fig. 12). In the UV/TiO_2 system, the degradation rate constants with a light intensity of 20, 100, and 400 W are 8.3×10^{-3}, 0.012, and 0.031 min^{-1}, respectively, which are much less than the corresponding constants in the $UV/H_2O_2/TiO_2$ system (0.054, 0.223, and 0.533 min^{-1}, respectively).

Apparently, UV light intensity has a positive effect on the rate of phenol photodegradation. This could be realized by the fact that increasing light intensity enhances the formation of hydroxyl radicals *via* H_2O_2 photodissociation. Moreover, adding H_2O_2 into the system improves the rate of phenol photodegradation by making more H_2O_2 available in system to undergo photodissociation; likewise, favors formation of hydroxyl radical. As shown in Fig. 13, an acceptably good linear correlation exists between the apparent first-
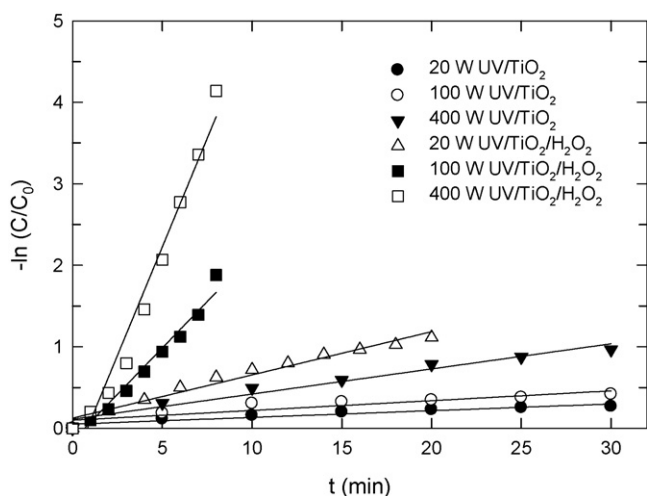

Fig. 12. Rate of phenol degradation at 25 °C and different UV light intensities ($C_0 = 0.36$ mM, initial pH 6.8, 1.20 mM H_2O_2).
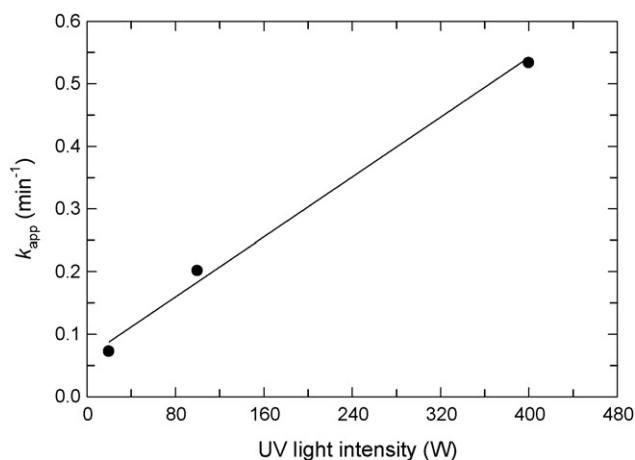

Fig. 13. Relationship between light intensity and the apparent first-order rate constant using $H_2O_2/TiO_2/UV$ process ($C_0 = 0.36$ mM, initial pH 6.8, 1.20 mM H_2O_2, 1 g/L TiO_2).

order rate constant and light intensity ($R^2 = 0.9892$) under the ranges studied, indicating the significance of UV light intensity in such photodegradation processes, at least for phenol.

4. Conclusions

The combined use of TiO_2 photocatalyst, H_2O_2, and UV light could greatly enhance the efficiency of phenol degradation. Photodegradation with $H_2O_2/TiO_2/UV$ process was much more effective than that with either TiO_2/UV or H_2O_2/UV process alone. Moreover, H_2O_2/UV process was slightly effective than TiO_2/UV process in degrading phenol due to the high electron/hole recombination rate on the TiO_2 surface, whereas H_2O_2 readily produced hydroxyl radicals under UV irradiation, thereby increasing photodegradation. On the other hand, phenol was attacked by both UV photo and hydroxyl radicals generated from H_2O_2. At a dosage of 1.0 g/L of Degussa P-25 TiO_2 under 400-W UV irradiation, e.g., phenol photodegradation increased from 56.4 to 94% due to the addition of 1.77 mM H_2O_2. The apparent first-order rate constant increased nearly three-fold compared to the absence of H_2O_2. The present results indicated that photodegradation of phenol using TiO_2 was best achieved near pH 7.4. Also, UV light intensity had a positive effect on phenol degradation.

According to the TOC measurements, phenol degradation by TiO_2/UV and H_2O_2/UV showed different behaviors. The reduction of TOC was gradual first and became sharp during the course of TiO_2/UV process whereas it was in reverse during the course of H_2O_2/UV process. Unlike the complete degradation of phenol (0.13 mM, pH 6.8) by 1 g/L TiO_2/UV within 1 h based on phenol concentration data, for example, the TOC of the solution was reduced by 92% only within 8 h. These results indicated that more time was required to completely mineralize phenol into water and carbon dioxide by photocatalysis.

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